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TITLE Partial Pressure Analysis of CF_4/O_2 Plasmas

AUTHOR(S): Martz, J.C.   MST-13
Anderson, W.E.   MST-13

Hess, D.W.   UC Berkeley

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Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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PARTIAL PRESSURE ANALYSIS OF CF$_4$/O$_2$ PLASMAS

J.C. Martz, D.W. Hess
Department of Chemical Engineering
University of California, Berkeley, Berkeley, CA 94720

W.E.Anderson
Materials Science and Technology Division
Los Alamos National Laboratory, Los Alamos, NM 87545

1. INTRODUCTION

Recently, reactive low-pressure RF glow discharges (plasmas) have become indispensable tools in the fabrication of microelectronic devices. However, despite the widespread use of glow discharges, a fundamental understanding of gas-phase and surface reaction mechanisms is generally lacking. Many diagnostic techniques exist for plasma analysis including optical emission and absorption spectroscopy[1,2], laser-induced fluorescence[1,5], and mass spectroscopy[3,4,6]. Of these methods, mass-spectroscopy offers the advantages of simple yet sensitive detection of both intermediate radicals within the discharge (flux analysis) and stable discharge products downstream (partial-pressure analysis). In addition, the data may be easily quantified to yield reactant and product partial pressure information within the discharge.

This work will examine a simple down-stream sampling arrangement for effluent analysis in a typical plasma environment. This method offers the advantage of simplicity when compared to the need for extraction optics and energy analyzing stages required for flux-type analysis[6]. In addition, partial pressure analysis provides information on the plasma/surface interactions occurring over the entire surface area of the reactor as opposed to just those occurring at the sampling orifice in flux-type analysis. This fact makes partial-pressure analysis particularly attractive for such tasks as plasma-etch end-point monitoring. In this example, experimental partial-pressure measurements of a CF$_4$/O$_2$ plasma are presented as is the application of the technique to plasma etch end-point detection.

2. TECHNIQUE

The parallel plate plasma reactor used in this study has been described elsewhere[7]. A Varian model 951 variable leak valve is installed in the pumping line to allow differential sampling of the effluent gas into a Balzers QMG 420 Quadrapole mass spectrometer. Sampled effluent is passed to the spectrometer by a 50 cm UHV bellows connected to the sampling valve. Chamber pressure is maintained at 80 mtorr while the quadrapole pressure is held at 1.0×10^{-5} torr by varying the leak rate through the sampling valve. Cathodic ionization voltage is set to 70 V while the dynode-type electron multiplier is held at 1500 V. The spectrometer is operated in a multiple-ion dynamic detection mode at a scan rate of 1 cycle/second.

Identification of the peaks from a scan of a typical CF_4/O_2 plasma shows the major products to be CO, CO_2, COF_2, F_2, HF, and numerous higher-ordered fluorocarbons. Each of these species, as well as the parent CF_4 and O_2 gases, were dynamically monitored as various plasma parameters were changed. Data from m/e of 19 and 20 exhibited long (several-minute) time constants after any change in plasma parameter. Indeed, the problems of measuring atomic fluorine have been well documented[4], particularly when measurements are performed in a downstream configuration. In addition, a fluorine mass balance (using the calculation described below) fails to account for more than 2/3 of the fluorine in the parent CF_4 gas. These problems illustrate the difficulty in measuring reactive, non-stable species in a downstream configuration. As such, this technique is only reliable when measuring stable species concentrations.

Values for the conversion of CF_4 and O_2 are calculated from

$$\%conversion = 100[(I_{off}-I_{on})/I_{off}] \qquad (1)$$

where I_{off} is the measured ion current with no plasma ignition and I_{on} is the average ion-current at the point of interest. This method is accurate provided that chamber partial pressure is linearly proportional to the measured ion-current value. Calibration of the product signals is a bit more elaborate; the method employed is similar to previous approaches[3] where the partial pressure is derived from the expression

$$I_i = p_i o_i T_i \qquad (2).$$

In eqn.(2) I_i is the measured ion current of species i, p_i the partial pressure, o_i the ionization cross-section, and T_i the product of the transmission coefficient, t_i and the flow coefficient K_i. Equation (2) assumes that no mass interference is present, although even if this were the case, a simple set of algebraic, linear equations is obtained which can be solved for p_i when I_i, o_i, and T_i are known. The ionization cross-section, o_i, for the species involved is taken from the literature[8,9]. In the case where a value is not available, o_i is extrapolated from the S value of reference (10), defined as the relative intensity of the strongest peak in the mass spectra cracking pattern as compared to nitrogen. The calibration factor T_i is assumed to have the form

$$T_i = Ae^{Bm_i} \qquad (3)$$

thereby allowing T_i to be calculated from the mass of species m_i provided the calibration constants A and B are known. A and B are calculated for each data series by using the measured ion-currents and the known plasma-off partial pressures for CF_4 at m/e of 69 and O_2 at m/e of 32.

Two methods allow a check for data consistency. The first involves summing the partial pressures of all species in the effluent and comparing this calculated total pressure to the known value of 80 mtorr. In our case, this calculation reveals that 75% of the data fall within a range of 74 to 81 mtorr, corresponding to an error of approximately 8%. The remaining data vary between 70 and 84 mtorr, or an error of 13%. This method, however, does not yield an error value for the individual peaks, but

simply provides an overall check on the thermodynamic consistency of the measured values. The second method involves performing atomic mass balances for each of the three atomic species in the system: C, O, and F. An overall carbon balance shows a worst-case discrepancy which amounts to 15% of the total carbon species present. Similarly, an oxygen balance yields a worst-case discrepancy of 30%. The results for fluorine have been discussed. When all sources of error are considered, the measured mole fractions of CO, CO_2, and COF_2 are within a factor of 2 of their actual values. The measurement of the variation in partial pressure or conversion for each species is accurate within 10% across the entire measurement range.[11]

3. RESULTS

Figures 1 shows the variation in reactant conversion and product mole fraction as a function of oxygen concentration for a 100 W CF_4/O_2 plasma.
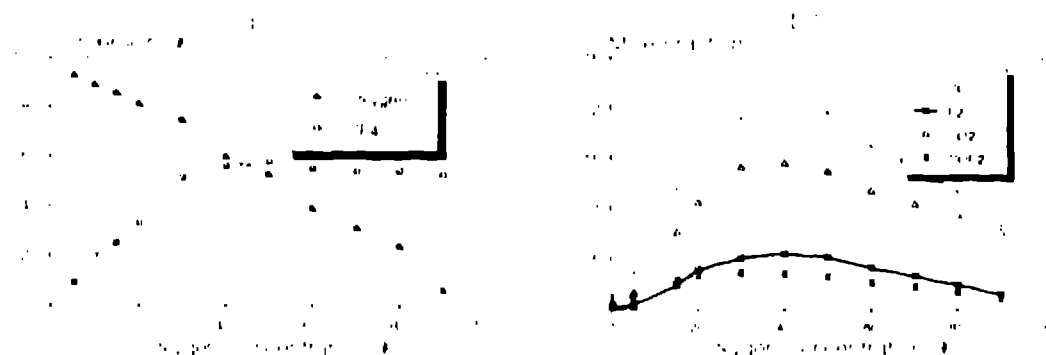

FIGURE 1. a) Conversion of O_2 and CF_4 versus oxygen concentration at a total flow rate of 8 sccm and differential power of 100 W. b) Gas-phase mole fraction of products versus oxygen concentration

These results are in good agreement with a similar flux-type analysis by Smolinsky and Flamm[4]. This data is intended only to illustrate the measurement technique. Complete results of this study, including a detailed analysis of the gas-phase chemistry, are available elsewhere.[7]

Figure 2 shows the variation in reactant conversion during the etching of a tungsten/silicon dioxide/silicon "sandwich". It is well known that the etching of tungsten in CF_4 proceeds by the consumption of CF_x radicals (x = 2 or 3) on the reactive surface. This fact is easily seen in the data as a shoulder in the CF_4 conversion up to a time of 7 minutes (the tungsten etch-through point), and a corresponding decrease in the O_2 conversion. This decrease in O_2 conversion is a direct result of a decrease in available CF_x, the species which reacts nearly exclusively with oxygen to yield the various products seen in figure 1b.[12] Further, the oxygen conversion increases as the etching process continues through the silicon dioxide layer, and ultimately reaches its highest value as the reaction proceeds into the oxygen deficient substrate silicon.
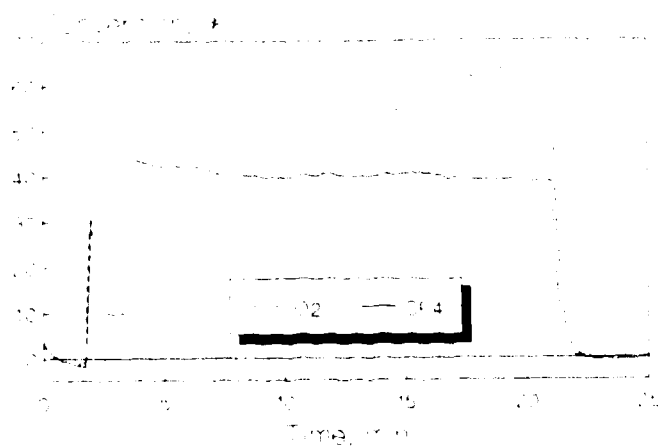
Figure 2. Monitor of conversion of O_2 and CF_4 as 5 in. diameter tungsten/SiO_2/Si wafer is etched. W thickness = 50 nm, thermal SiO_2 thickness = 30 nm. Pressure = 80 m⋅orr, Power = 100 W. 20% Oxygen at 8 sccm total flow. (system residence time = 14.7 s)

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